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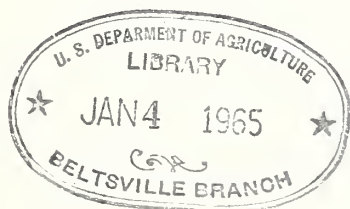
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# Radiocarbon Dating by Liquid Scintillation Spectrometry:

## Synthesis of Benzene ($C_6^{14}H_6$)

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# Radiocarbon Dating by Liquid Scintillation Spectrometry: Synthesis of Benzene $(C_6^{14}H_6)$[1]

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## ABSTRACT

The measurement of natural carbon-14 by liquid scintillation has received much attention in recent years. The major difficulty has been the routine synthesis of compounds suitable for liquid scintillation counting.

This paper describes in detail the chemical synthesis of benzene from the original carbon sample. Benzene, containing 92.26 percent carbon, is an ideal solvent for scintillation counting. The sample is converted to carbon dioxide by combustion or acidification and the evolved carbon dioxide is collected in ammonium hydroxide. Strontium carbonate is precipitated from the ammonium carbonate solution upon addition of strontium chloride. The carbonate is reduced to carbide by reaction with magnesium metal. Acetylene is produced by reacting the carbide with water. The acetylene is converted to benzene by the catalytic process employing diborane-activated silica-alumina. Benzene of scintillation quality is produced with an overall carbon yield of 50 to 60 percent. The sample can be synthesized and counted in 1 week.

Diborane used in the activation of the silica-alumina is produced in a hood-mounted manifold by the reaction of sodium borohydride and boron trifluoride etherate. The purified diborane gas is passed, in a continuous process, into columns containing the silica-alumina. Activation is necessarily conducted in an oxygen- and water-free atmosphere.

## INTRODUCTION

The radiocarbon dating technique has received worldwide attention by archeologists and geologists since the discovery of natural radiocarbon by Libby and his associates (3, 4, 26, 27).[3] Since the development of the method by Libby, much effort has been expended to improve the accuracy and precision of the values (dates) obtained from the various materials.

The low specific activity and low energy of the beta emissions from carbon-14 make it necessary to use highly sensitive and efficient detection equipment. Prolonged counting is necessary to reduce the statistical errors arising from the radioactive decay process. Intensive investigations have been conducted to determine methods for minimizing the background counting rates for the various detection systems. Emphasis has been placed not only on extending the maximum age that can be determined, but also on improving the precision and accuracy for samples only a few hundred years old.

The original, solid counting system devised by Libby has been largely replaced by gas counting systems. Liquid scintillation counting has, however, received more attention in recent years. The major difficulty has been the synthesis of compounds that are suitable for liquid scintillation counting. This paper presents a detailed procedure for the synthesis of benzene, an ideal solvent for scintillation counting, from the original sample carbon. This solvent is particularly suitable for laboratories employing commercial liquid scintillation spectrometers having minimal shielding.

# PREVIOUS WORK

## Solid Counting System

The original method employed solid elemental carbon synthesized from the sample and a special Geiger-Mueller tube, known as the "screen wall" counter (25, 28). The system was surrounded by an anti-coincidence ring of Geiger-Mueller tubes arranged to minimize the background counting rate. The arrangement permitted alternate counting of the background and sample without removing the sample from the counter. This advantage has been lost in subsequent counter designs. Low counting efficiencies ($\sim$ 5 percent) and likelihood of sample contamination were the major limitations of this method.

## Gas Counting Systems

Gas counting systems employing Geiger or proportional counting tubes have largely replaced the "screen wall" counter. These systems use carbon dioxide (9, 16, 17, 18, 20), acetylene (14, 40), or methane (13, 19) as the counter gas. The self-absorption effect present in the solid carbon method is eliminated. Counting efficiencies of 70 to 95 percent are characteristic of these systems. The low density of these gases, however, restricts the sample mass. Some laboratories have overcome this problem by (a) counting the gases at higher pressures (2 and 3 atmospheres), and/or (b) employing large counting tubes (5- or 6- liter capacity) combined with extensive selected shielding. A typical system is shielded by layers of several inches of selected lead, mercury, iron, and paraffin with boric acid. Cosmic-ray guard counters arranged in anti-coincidence are also provided to lower the background counting rate. Extensive gas purification is conducted to eliminate quenching of the counter gas. High-vacuum equipment is necessary for handling the gases during purification.

The gas counting systems have been primarily custom built and have been designed to provide highly stable electronic and detection systems. Stability of the electronic components of the counting system combined with ease of sample preparation has resulted in the gas counting method being the most common one used for radiocarbon dating.

## Liquid Counting Systems

The recent development of liquid scintillation spectrometry offers a new and third approach to carbon-14 counting. Bluh and Terentiuck (8), in 1952, may have been the first to propose the use of liquid scintillation counting of natural carbon-14. This method was also suggested by Hayes, Williams, and Rogers (23) in 1953. The major problems associated with this technique are (a) the synthesis of compounds suitable for liquid scintillation counting, and (b) the relatively high background counting rates associated with commercial liquid scintillation spectrometers.

The compounds synthesized from the sample carbon must meet the following requirements: (a) be suitable for dilution with a standard solvent system, or be a suitable solvent itself (for incorporation of scintillators); and (b) be free from chemical- and light-quenching compounds. In addition, the compounds should contain a large percentage of carbon from the original sample. These conditions restrict the number of compounds suitable for carbon-14 dating. Nevertheless, several compounds meeting these requirements to varying degrees have been synthesized and used in radiocarbon dating programs.

## Diluents

Methanol was apparently the first useful diluent for routine carbon dating (15, 21, 35). Yields exceeding 70 percent can be obtained by the reduction of carbon dioxide (31). Ethanol was also synthesized by Arnold (5) and successfully used in carbon dating. Both methods are characterized by simple chemical syntheses but suffer in that they possess severe scintillation quenching properties. The amount of original-sample carbon which can be successfully incorporated into the counting system is, therefore, limited.

Trimethyl borate was synthesized by Pringle, Turchinetz, Funt, and Danyluk (36) and used as a diluent in a benzene-naphthalene solvent system. The synthesis is only slightly more difficult than that of methanol. It has the advantages of containing a larger percentage of original-sample carbon and causing less chemical quenching than methanol.

Paraldehyde has been successfully employed as a diluent by Leger and Pichat (24). Acetylene is converted to paraldehyde with an overall yield of 30 percent. All six carbons are derived from the sample. The diluent can be added in large quantities to the solvent system. The counting sample employed by Leger and Pichat contained 39 percent original-sample carbon.

Arnold (5) has routinely used hexane-octane as the diluent in a radiocarbon dating program. The mixture is synthesized by polymerization of acetylene over cuprous chloride with subsequent hydrogenation to hexane-octane. The synthesis is complex and the yields are about 30 percent. The ratio of hexane to octane varies and each product must be analyzed for carbon content. The mixture can be added in large quantities to the solvent system. Furthermore, it has been shown by carbon-13 measurements that isotopic fractionation in the synthesis is only slight (22).

Two gases readily synthesized from the original carbon sample have been used as diluents in a toluene solvent system. Carbon dioxide was used by Barendsen (7) with a counting efficiency of 30 percent. Counting was conducted at $-20^{\circ}$ C. in a glass vial especially constructed to withstand the high pressure of the system. Audric and Long (6) found that large quantities of acetylene could be incorporated into toluene containing 2 percent ethanol at $-75^{\circ}$ C. The obvious simplicity of chemical synthesis renders these methods most attractive for the radiocarbon dating technique. However, the quenching properties of these diluents combined with the difficulty of handling these materials under pressure have apparently prevented them from being applied in routine dating. Further investigations using carbon dioxide as a diluent in various solvent-scintillator systems would seem very profitable.

## Solvents

Toluene, an ideal solvent for liquid scintillation counting, was synthesized by Funt and co-workers (21, 35). Sample carbon was incorporated into the alkyl group of the toluene molecule. This approach was more expedient than synthesizing toluene containing seven sample carbon atoms per molecule. The method resulted in an excellent solvent; however, it contained only 13 percent original-sample carbon. The synthesis was described as "somewhat involved for routine measurements of large numbers of samples."

The synthesis of ethylbenzene as a solvent was reported by Starik and associates (39). Apparently, two carbon atoms per molecule were derived from the original-sample carbon. The solvent was counted at 31 percent efficiency; an absolute specific activity of 15.2 disintegrations per minute per gram (d/m/g) was obtained for contemporary carbon.

Benzene, like toluene, is an excellent solvent for liquid scintillation counting. Recently its synthesis has been the subject of many investigations. Pichat (33), and Pichat and Baret (34) investigated the polymerization of acetylene to benzene, using Reppe's catalyst (37). This method was rejected, however, because of the problems associated with handling acetylene at high pressures.

Tamers and coworkers (41, 42) synthesized benzene by pyrolysis of acetylene at 600° C. Benzene produced in the reaction was removed by cold traps. The unreacted acetylene, maintained at a pressure near one atmosphere, was passed continuously into the pyrolysis tube. The benzene product was chemically purified by distillation. An overall carbon yield of 30 percent was obtained in the synthesis of benzene from carbon dioxide.

Shapiro and Weiss (38, 43) polymerized acetylene to benzene by a catalytic process in which the acetylene was passed over silica-alumina catalyst (Type S-46; Houdry Process Corp., 1528 Walnut Street, Philadelphia, Pa.[4] ) previously activated with diborane gas. Noakes, Hood, and Isbell (29, 30) modified this procedure to synthesize scintillation-quality benzene on a routine basis for carbon-14 dating. Benzene was produced in 50 percent carbon yield. Diborane gas was obtained from the Callery Chemical Co., Marketing Division, 9600 Perry Highway, Pittsburgh 37, Pa. This general method is now employed in routine carbon-14 dating laboratories at the Texas Agricultural and Mechanical College and at the University of Texas.

The detailed method described herein is a modification of the basic method employing diborane-activated silica-alumina catalyst for the cyclization of acetylene to benzene. The basic method has been extended to include the generation of high-purity diborane and its subsequent introduction to the silica-alumina catalyst for activation of the latter.


# MATERIALS AND METHODS


## General Considerations

Benzene, synthesized from the sample carbon, was selected as the solvent because it is the most favorable scintillating solution for carbon-14 dating with the liquid scintillation spectrometer available at the USDA Sedimentation Laboratory. Benzene is an ideal solvent for scintillation counting. It contains 92.26 percent carbon, all of which is derived from the original carbon sample. Hence, a large amount of carbon can be incorporated into a sample of small volume for counting. Sample size is extremely important in low-level counting programs employing commercially available liquid scintillation counters.

The method of cyclizing acetylene to benzene using diborane-activated silica-alumina was selected because it produces benzene of scintillation grade without further purification.

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[4] Trade names are used in this publication solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or an endorsement by the Department over other products not mentioned.

# General Method

The general method for the synthesis of benzene from the original sample is given by the following reactions:

1. $Sample + O_2 \longrightarrow CO_2 + H_2O$

2. $CO_2 + 2NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$

3. $(NH_4)_2CO_3 + SrCl_2 \longrightarrow SrCO_3 + 2NH_4Cl$

4. $2SrCO_3 + 5Mg \longrightarrow SrC_2 + SrO + 5MgO$

5. $SrC_2 + H_2O \longrightarrow C_2H_2 + SrO$

6. $3NaBH_4 + 4BF_3(C_2H_5)_2O \xrightarrow{\text{Diglyme}} 2B_2H_6 + 3NaBF_4 + 4(C_2H_5)_2O$

7. $3C_2H_2 \xrightarrow[\text{silica-alumina}]{B_2H_6-\text{activated}} C_6H_6$

# Chemical Procedures

Details of the method of benzene synthesis employed at the USDA Sedimentation Laboratory are presented in the following sections.

## Pretreatment of Sample

All samples to be dated are visually inspected for contaminants. Obvious contaminants are removed from the sample before chemical pretreatment. Wood and charcoal are washed with hot 3N sodium hydroxide (NaOH), distilled water, hot 3N hydrochloric acid (HC1), and finally with distilled water. Samples of peat, soil, and animal residues, sample size permitting, are subjected to a more rigorous pretreatment resulting in the separation of crude fractions of "cellulose" and "lignin."

Standard methods employed by wood chemists have been adopted for isolating the "cellulose" and "lignin" fractions (32, 44). The gross sample is boiled in distilled water to remove sugars and salts. The sample is then divided into two fractions for further treatment. Fraction A is treated with 75-percent sulfuric acid ($H_2SO_4$) at $10^0$ C. for 24 hours to dissolve the cellulose. The resulting crude "lignin" fraction is washed free of excess acid (by centrifugation) and dried in an oven for subsequent combustion. Lignin dissolution is conducted on fraction B by treatment with an acidified solution of sodium chlorite ($NaC1O_2$). The reaction is performed at about $70^0$ C.; approximately 0.3 gram of sodium chlorite is added per gram of sample (dry weight basis) every hour for a period of 5 hours. During the digestion, the solution is maintained at about pH 2 by the addition of HC1 as needed. The crude cellulose residue obtained from this reaction is washed with distilled water (by decantation and centrifugation) to remove excess salts. After being dried in an oven, the sample is ready for combustion.

Shells and bones are scrubbed vigorously with a steel brush and treated with $\sim$1N phosphoric acid ($H_3PO_4$) in an attempt to remove surface contaminants (carbonate and others). The sample is washed in distilled water, dried, and stored for later conversion to carbon dioxide by acidification with $H_3PO_4$.

## Conversion of Sample to Carbonate

The combustion of non-carbonate samples (fig. 1) and the purification and collection of carbon dioxide (fig. 2) are necessarily conducted as a continuous process. The sample is placed in the inner Vycor 7900 tube (41 mm. O.D. x 500 mm. long). This (sample) tube is enclosed within another Vycor 7900 tube (51 mm. O.D. x 1,500 mm. long). Air is removed from the system by a vacuum pump and replaced with helium (He), via valve 1, to approximately atmospheric pressure. The sample is then charred in the helium atmosphere. Volatiles from the sample are moved through the tip of the inner tube (downstream end) and ignited on the quartz wool by purified tank oxygen ($O_2$) admitted through valve 2. The charred sample is then burned in a conventional manner. The sample is ignited within the inner tube (downstream end) by introducing oxygen through valve 1 and applying heat externally with a hand torch. Additional oxygen, if needed, is supplied through valve 2. Check valves are placed in the oxygen lines to prevent absorption of any sample carbon dioxide ($CO_2$) by the Ascarite, should reversal of the gas flow occur as a result of pressure changes in the system. Any carbon monoxide (CO) present is oxidized to carbon dioxide in the copper oxide (CuO) furnace ($750^\circ$ C.).

The temperature of the gas stream is reduced at the downstream end of the outer tube by a water-cooled coil which surrounds the outer tube, and by glass wool packing, through which the gases must pass.

The gas stream consists primarily of $CO_2$, $H_2O$, and excess $O_2$. Traces of nitrogen ($N_2$), sulfur dioxide ($SO_2$), and halogens are also present. The bulk of the water vapor is trapped out at the downstream end by an ice-water slush.
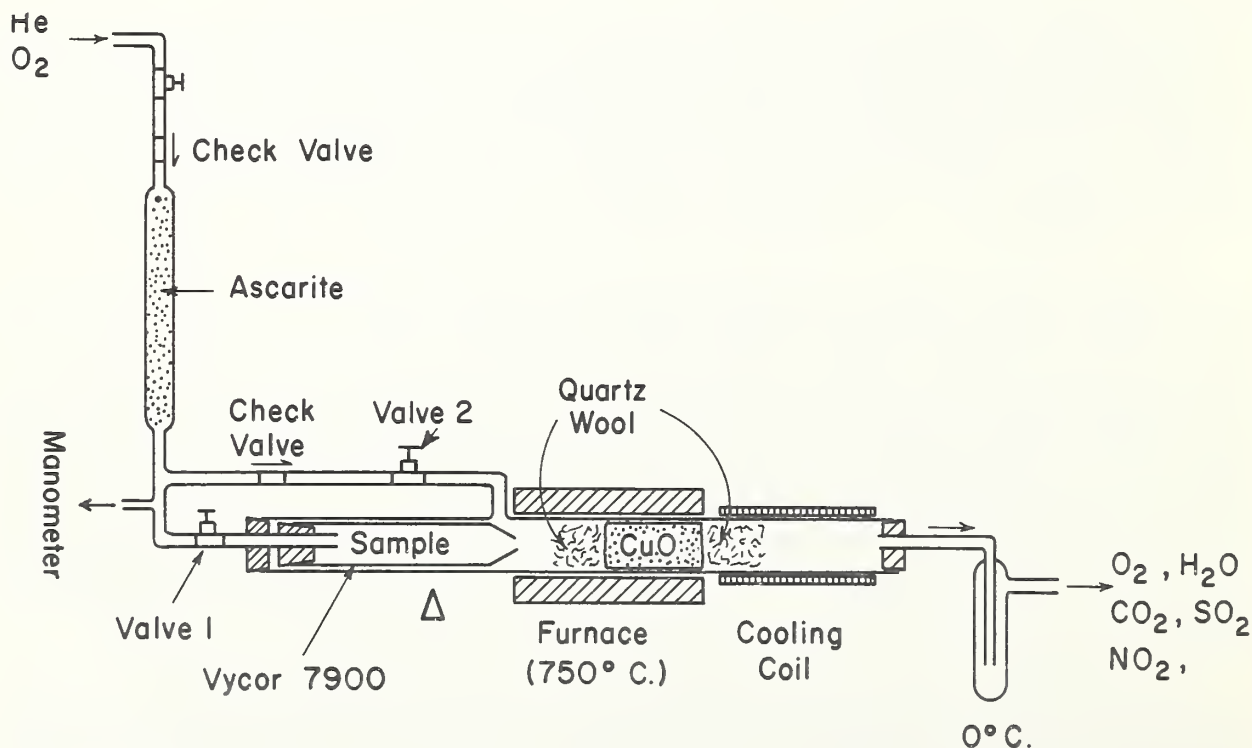


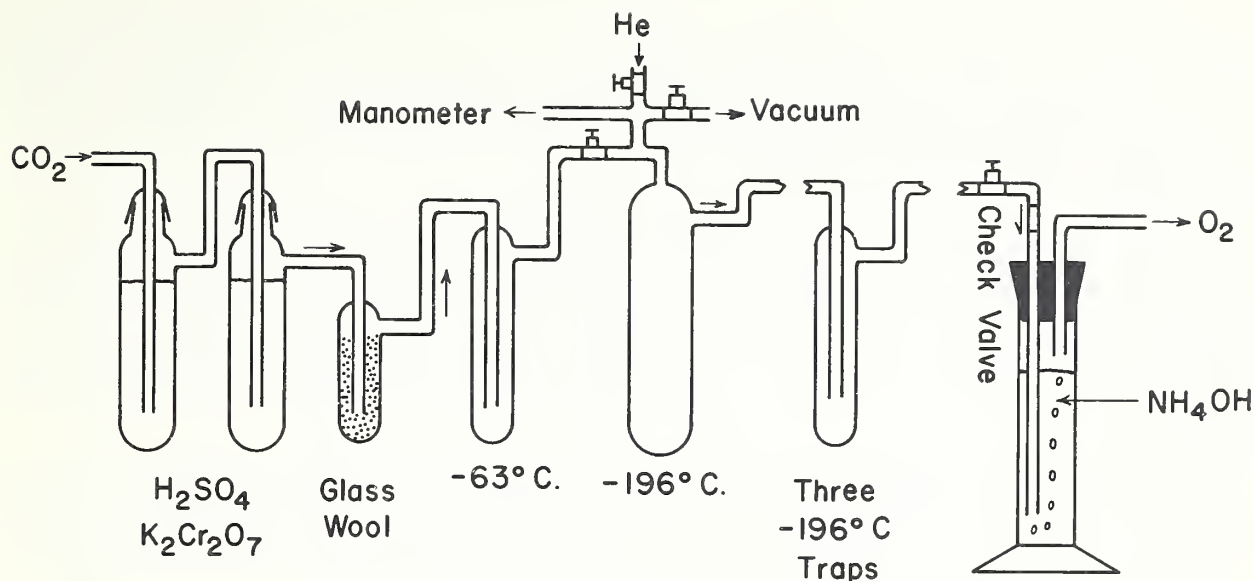Figure 1.--Apparatus for combustion of sample.

Figure 2.--Apparatus for purification and collection of carbon dioxide.

Figure 2 shows in schematic form the system for purification and collection of the $CO_2$. The sulfuric acid-potassium dichromate ($H_2SO_4$ - $K_2Cr_2O_7$) solutions oxidize $SO_2$ to $SO_3$, with subsequent absorption, and remove traces of water vapor. Carbon dioxide is frozen out at liquid nitrogen temperature (-196° C.) while excess oxygen is removed by the vacuum pump. After completion of combustion, the liquid nitrogen (-196° C.) traps are removed and the solid $CO_2$ is permitted to sublime into a 15-percent solution of ammonium hydroxide ($NH_4OH$). The ammonium hydroxide absorption column (60 mm. O.D. x 1,200 mm. long) provides a travel path of 900 mm. for absorption of the $CO_2$. The gaseous $CO_2$ is partially purified by passage through -63° C. (chloroform-liquid nitrogen slurry) traps before entering the $NH_4OH$.

Original carbonate samples are handled in a different manner. These are reacted with $H_3PO_4$ and the evolved $CO_2$ is partially purified by passage through -63° C. traps into $NH_4OH$.

The ammonium carbonate [$(NH_4)_2CO_3$] solution formed by the reaction of sample $CO_2$ and $NH_4OH$ is transferred from the absorption column to a 4-liter flask or beaker. Strontium carbonate ($SrCO_3$) is precipitated from the $(NH_4)_2CO_3$ solution by adding strontium chloride ($SrCl_2$) and subjecting the mixture to a vigorous digestion period. The precipitate is permitted to settle and the supernatant is removed by suction through a large filter stick (90 mm. O.D.). Distilled water is then added to the precipitate and the digestion is repeated. Four or five washings are usually adequate for removal of ammonium chloride ($NH_4Cl$) and excess $SrCl_2$. The washing procedure is terminated when chlorides are no longer detectable in the wash solution (sliver nitrate test). The $SrCO_3$ is dried at 105° C. and then heated to 500° C. to remove traces of ammonia.

## Conversion of Carbonate to Carbide

Strontium carbonate is reduced to strontium carbide ($SrC_2$) by reaction with magnesium (Mg) metal. This solid state reaction is conducted in a stainless steel cylinder at high temperature. The basic procedure is the same as that employed by Suess (40).

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The $SrCO_3$ is ground with mortar and pestle to a fine powder. Magnesium (Mallinckrodt No. 5894 Mg powder) is mixed thoroughly with the $SrCO_3$ in the ratio 1:1.3 by weight. This mixture is then transferred to a stainless steel reaction cylinder (60 mm. O.D. x 460 mm. long with a 3-mm.-thick wall). The reaction cylinder is connected to the upper ballast cylinder by stainless steel bolts (fig. 3). An asbestos gasket placed between the two cylinder flanges provides a vacuum-tight seal.

The connected cylinders are clamped into place in an enclosed hood. The system is evacuated for at least 1 hour. Because it is imperative that the system be free from leaks, frequent checks are made to confirm that the assembly is leakproof. Helium gas, dessicated by slowly being passed through a $-196^\circ$ C. trap, is then introduced into the cylinders to a positive pressure of 30 cm. Hg. The cylinders are again evacuated; evacuating and purging with He is repeated four times before the solid state reaction is initiated. The overall time required for the evacuations and the introductions of He is usually about 3 hours.

After the final evacuation, the entire surface of the reaction cylinder is heated to about $200^\circ$ C. with oxygen-gas torches. The vacuum pump is operated during the heating period to remove traces of water vapor and air.

Drying the Mg-$SrCO_3$ mixture at a low temperature ($110^\circ$ C.) has been found desirable, but only if conducted in a vacuum or in an atmosphere of inert gas. Drying the mixture in air results in an oxide formation on the surface of the Mg metal; the result is a sizable reduction in yield of $SrC_2$. Yields of $SrC_2$ have been reduced by 25 to 40 percent by the use of Mg metal dried in air at $110^\circ$ C. for 3 hours.
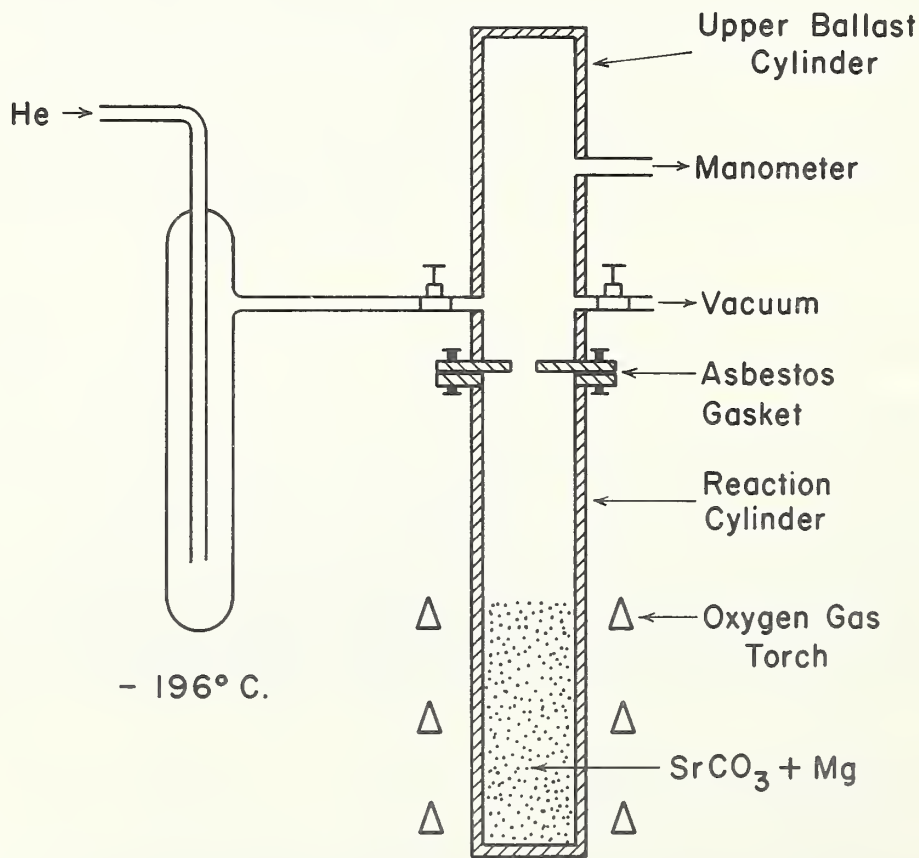


Figure 3.--Apparatus for reduction of strontium carbonate.

After the water vapor and air are thoroughly removed from the cylinders, the $Mg$-$SrCO_3$ mixture is ready for reaction. The vacuum pump is removed from the system and intense heat ($1,000^\circ$ to $1,500^\circ$ C.) is applied with the gas-oxygen hand torches to the reaction cylinder at the upper level of the $Mg$-$SrCO_3$ mixture. The reaction is highly exothermic, causing the cylinder to glow red at the point of reaction. The torches are gradually moved downward from the point of reaction to assist lower portions of the mixture to undergo reaction. In many cases the reaction will proceed downward with only slight assistance from the gas-oxygen torches. Upon completion, the lower portion of the reaction cylinder is bright red; the time of total reaction is usually 4 or 5 minutes. After completion of the reaction, dry He is introduced to the system and maintained at a slight positive pressure until the mixture has cooled to room temperature. Quantitative transfers of the contents of the reaction cylinder are now routinely made with a loss of only 1 or 2 percent of the original carbon.

The procedure described above has proved satisfactory for more than 50 reactions conducted at this laboratory. Some of the first reactions showed frequent, excessive pressure changes during the reduction process. These excessive pressures could be traced to insufficient evacuating and drying of the $Mg$-$SrCO_3$ mixture.

The presence of nitrogen compounds in the $Mg$-$SrCO_3$ mixture results in an unsafe reaction and usually in a reduction of the $SrC_2$ yield. The following steps have been introduced to insure the absence of these compounds:

   a. To remove traces of ammonia left from the precipitation reaction, the $SrCO_3$ is heated to $500^\circ$ C.

   b. To remove traces of nitrogen compounds from the reaction vessel, the cylinder is heated to $500^\circ$ C. in a muffle furnace or in a tube furnace. These nitrogen compounds are absorbed by the reaction cylinder during the cleanup procedure between ractions. Nitric acid ($HNO_3$), followed by conventional laboratory glass washing practices, is used to remove traces of Mg metal and carbide. Several rinses in distilled water have proven inadequate in removing all of the $HNO_3$. This contamination measurably reduces the $SrC_2$ yield. Reductions of 25 percent, and occasionally 50 percent, were encountered and directly attributed to this cleanup procedure. The presence of nitrogen and/or its compounds possibly leads to the formation of strontium nitride ($Sr_3N_2$) or strontium cyanamide ($SrCN_2$).

The system is designed for 80 to 120 grams of $SrCO_3$, but has been tested with 200 grams of $SrCO_3$ and the required amount of Mg metal.

## Conversion of Carbide to Acetylene

The contents of the reaction cylinder (gray-black carbide and unreacted Mg) are removed for further processing. The mixture is carefully ground, in the absence of water vapor, with a mortar and pestle. The mixture is then transferred to a 1-liter modified Erlenmeyer flask for storage, or for connection to the acetylene ($C_2H_2$) production apparatus (fig. 4). After the $C_2H_2$ production apparatus is evacuated, the carbide and unreacted Mg mixture is slowly added to water contained in a 2- or 4-liter side-arm flask. Acetylene is produced as shown in reaction 5 (p. 5). The reaction flask and contents are cooled in an ice water bath; the mixture of carbide and water is agitated by a large magnetic stirrer.

The acetylene gas produced is passed through charcoal and cold traps ($-63^\circ$ C.) to remove impurities and traces of water vapor before the acetylene is solidified in the liquid nitrogen ($-196^\circ$ C.) traps. Hydrogen ($H_2$) produced by the oxidation of unreacted Mg metal with water is
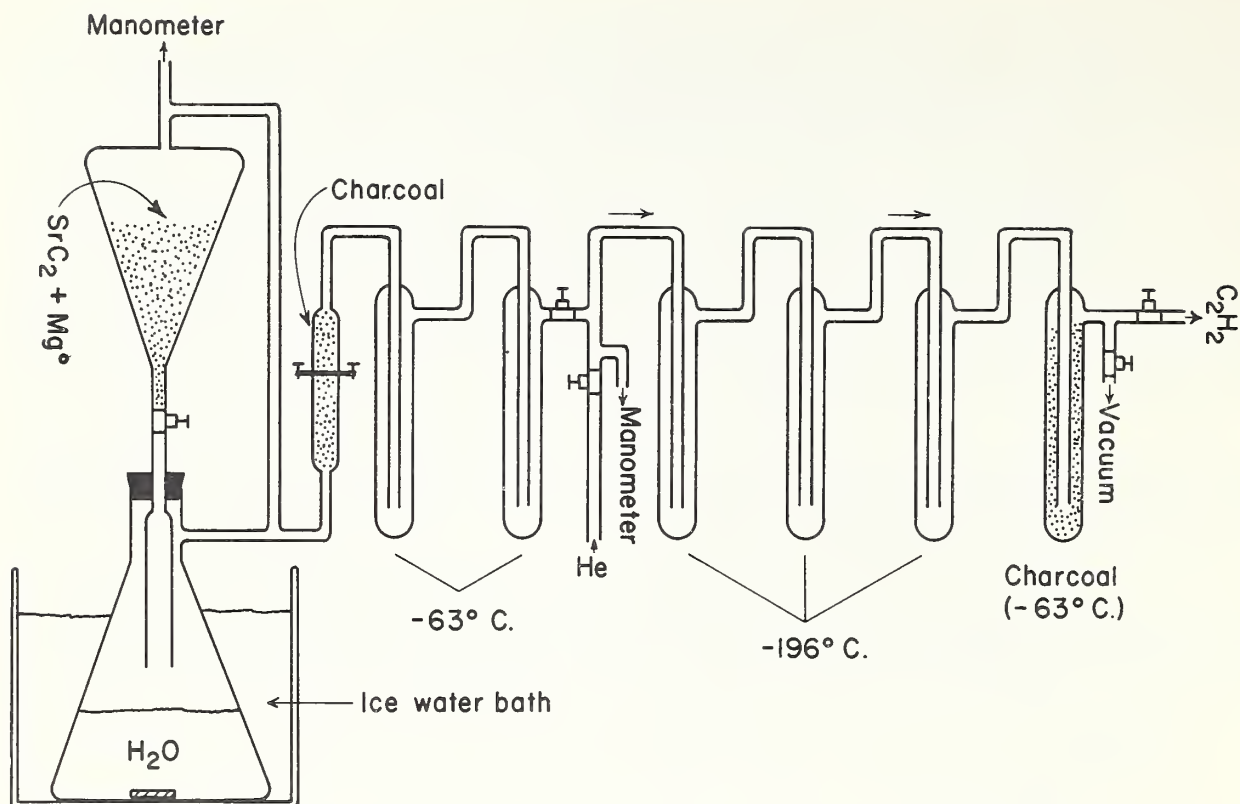
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Figure 4.--Apparatus for conversion of carbide to acetylene.

removed by the vacuum pump. Usually 15 to 30 minutes are required for the addition of the carbide mixture to the water. An increase of 10 to 20 percent in $C_2H_2$ yield is obtained, however, by constant stirring of the carbide-water mixture and an additional reaction time of one hour. Finally, hydrogen is removed by the vacuum pump. The $C_2H_2$ is permitted to sublime through $-63°$ C. traps containing cooled charcoal (40) into a previously evacuated 5- to 10-liter storage cylinder (see fig. 6). The pressure and temperature are recorded and the $C_2H_2$ yield is computed from the ideal gas law. Helium is admitted to flush traces of $C_2H_2$ from the reaction system into the storage cylinder.

## Activation of Silica-Alumina Catalyst with Diborane Gas

The silica-alumina (Type S-46) employed in the catalytic conversion of $C_2H_2$ to benzene ($C_6H_6$) is obtained from the Houdry Process Corp. Activation of the pelleted catalyst is conducted in Pyrex 7740 glass columns fitted with 29/42 ₮ joints and high-vacuum stopcocks. Various column sizes have been used, depending on the amount of $C_2H_2$ to be converted. The most commonly used activation column measures 41 mm. O.D. x 300 mm. in length. Both chromatographic and trap-styled columns have been employed. The columns are filled with about 200 grams of silica-alumina catalyst; the columns and catalyst are heated to $400°$ C. under a vacuum ($\sim 1$ mm. Hg) for three hours to remove associated water. The columns are then filled with dry He to a positive pressure of about 30 cm. Hg. After being cooled, the columns are placed in a special hood-mounted rack for activation with diborane gas.

The apparatus used for the production of diborane ($B_2H_6$) gas and subsequent activation of the silica-alumina is illustrated in figure 5. Ten activation columns are arranged in series for the most efficient use of the $B_2H_6$ during the activation process. The columns are interconnected
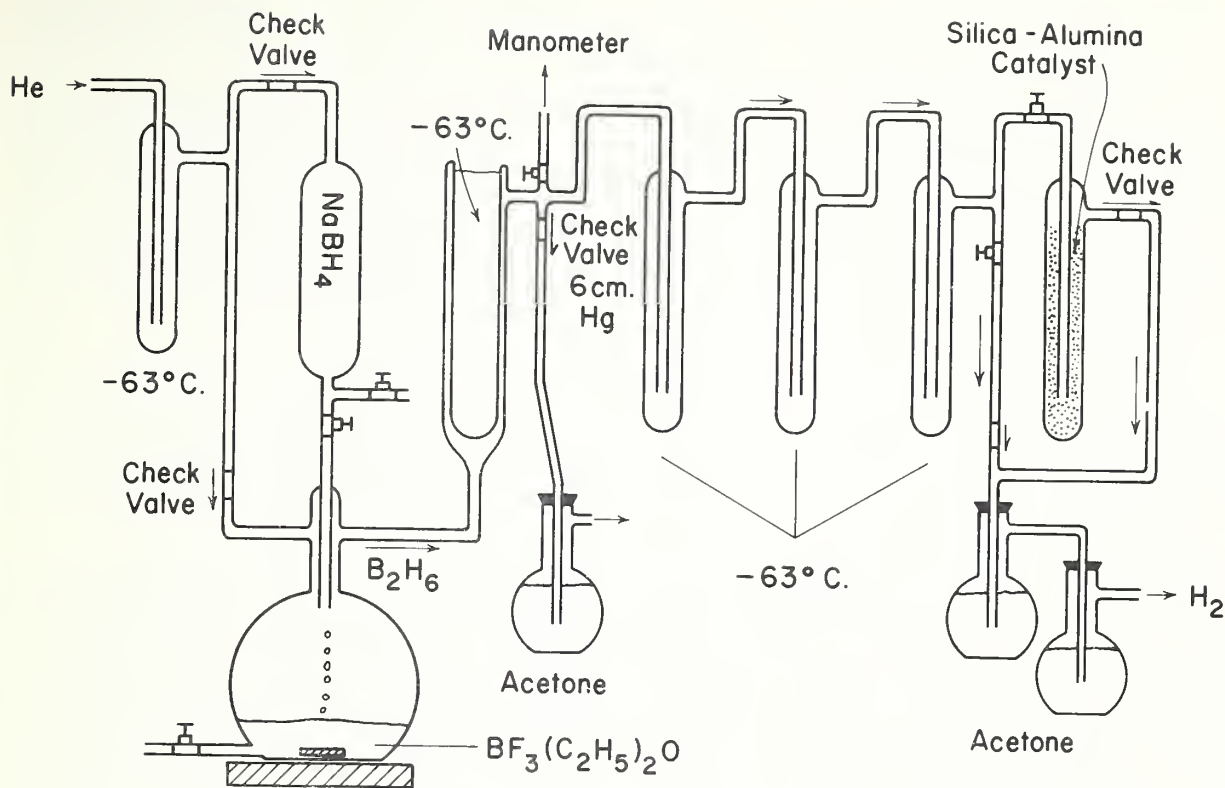
Figure 5.--Apparatus for production of diborane and activation of silica-alumina catalyst.

with Teflon or polyvinyl chloride tubing. The interconnections are T-shaped, permitting the removal of oxygen and water vapor by the vacuum pump before activation. The first column is connected to the main line of the $B_2H_6$ manifold. The last column is connected to the acetone waste flasks.

The apparatus is evacuated and dry He is introduced into the system. Waste lines and safety valves are purged to insure removal of oxygen and satisfactory operation of the check valves. Chloroform-liquid nitrogen slurry traps ($-63^\circ$ C.) are placed in position. The valves to each column are opened, after which dry He is introduced to insure that the column lines are open, and to remove oxygen and water from the waste lines downstream from the check valves.

Diborane is prepared in a helium atmosphere by the following reaction of sodium borohydride ($NaBH_4$) and boron trifluoride etherate [$BF_3(C_2H_5)_2O$] in diethylene glycol dimethyl ether (Diglyme):

$$3NaBH_4 + 4BF_3(C_2H_5)_2O \xrightarrow{\text{Diglyme}} 2B_2H_6 + 3NaBF_4 + 4(C_2H_5)_2O$$

This basic reaction is the same as that employed by Brown and coworkers (11, 12) for the generation of $B_2H_6$ in small reaction systems.

Commercial grade reagents without further purification are used in generating the $B_2H_6$. About 350 grams of $BF_3(C_2H_5)_2O$ in 500 ml. of Diglyme are added to the reaction flask (2,000-ml. capacity). The dropping funnel ($\sim$1,500-ml. capacity) is filled with a saturated solution of $NaBH_4$ in Diglyme ($\sim$1$\underline{M}$ solution at room temperature). The filling operations are conducted under

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vacuum or by forcing the solutions into their respective flasks under positive He pressure. Care is exercised to avoid mixing the reagents during the filling procedure.

The $NaBH_4$-Diglyme solution is added dropwise to the $BF_3(C_2H_5)_2O$-Diglyme solution. Adequate mixing of the reactants in the reaction flask is accomplished by a magnetic stirrer. A modified Dewar flask filled with a dry ice-acetone slurry or a choloroform-liquid nitrogen slurry is used to liquefy ethyl ether released during the reaction. The additional cold traps provide further purification of the $B_2H_6$ gas. Hydrogen released from the reaction of the $B_2H_6$ with the silica-alumina passes through the acetone waste flasks to the overhead-hood exhaust system. Unreacted $B_2H_6$ reacts with the acetone, forming diisopropoxyborane, $[(CH_3)_2CHO]_2BH$.

About 2 hours are required for generating the $B_2H_6$ ($\sim 1$ mole) and activating the silica-alumina. Check valves and poppet check valves (or Hg bubblers) are employed in the apparatus to provide control of direction of flow and safety of operation. A poppet valve equivalent to 6 cm. of Hg is located in the main line. If the pressure exceeds this value in the reaction system, the excess gas passes through the poppet valve to an acetone waste flask.

When all the $B_2H_6$ is generated, the gas stream is directed to the acetone waste system and the upstream valve on the first column is closed. The contents of the reaction flask are drained into the sewer line with the assistance of positive He pressure on the apparatus. Cold traps are lowered and the trapped products are permitted to escape to the acetone waste flask. Acetone is forced into the apparatus, under He pressure, to remove traces of $B_2H_6$ and ether products. The system is then washed with water before disassembling. Diborane, hydrogen, and breakdown products from the reaction of $B_2H_6$ and the silica-alumina are maintained at a positive pressure of 10 cm. Hg in the columns. Excess pressure is permitted to escape through a 10 cm. Hg bubbler to the acetone waste system. This reaction process is permitted to continue until the formation of $H_2$ and other breakdown products ceases. This often requires 24 to 36 hours for completion.

When the activation process is completed the columns are removed for further processing of the silica-alumina. The columns are heated to $150^o$ C. and evacuated to remove excess $B_2H_6$ and its reaction products. The columns are stored under a positive He pressure of about 20 cm. Hg. Columns prepared in this manner have been stored for six months without apparent loss in $C_2H_2$-to-$C_6H_6$ conversion efficiency. It is necessary to exclude oxygen and water vapor from the silica-alumina during its activation and subsequent storage.

## Conversion of Acetylene to Benzene

The activated columns are now ready for the catalytic conversion of $C_2H_2$ to $C_6H_6$. Acetylene is passed from the storage cylinder through dessicating cold traps (-$63^o$ C.) into a column containing $B_2H_6$-activated silica-alumina catalyst (fig. 6). The $C_2H_2$ is displaced from the storage cylinder by water admitted to the lower portion of the cylinder at a controlled rate. The pressure of the $C_2H_2$ gas in the storage cylinder is never permitted to exceed 95 cm. Hg. A poppet check valve (95 cm. Hg) is provided in the line to release any excess pressure that might develop as a result of trap freezeup or other restriction of the $C_2H_2$ flow.

Acetylene is passed into the $B_2H_6$-activated silica-alumina column at the rate of about 2 liters per hour. The conversion of $C_2H_2$ to $C_6H_6$ is an exothermic reaction characterized by a purple coloration of the silica-alumina at the site of reaction. The reaction front moves up the column until all of the catalyst has reacted or until all the $C_2H_2$ sample has been passed into the column. The stopcocks are then closed and the column is transferred to the $C_6H_6$ extraction apparatus.
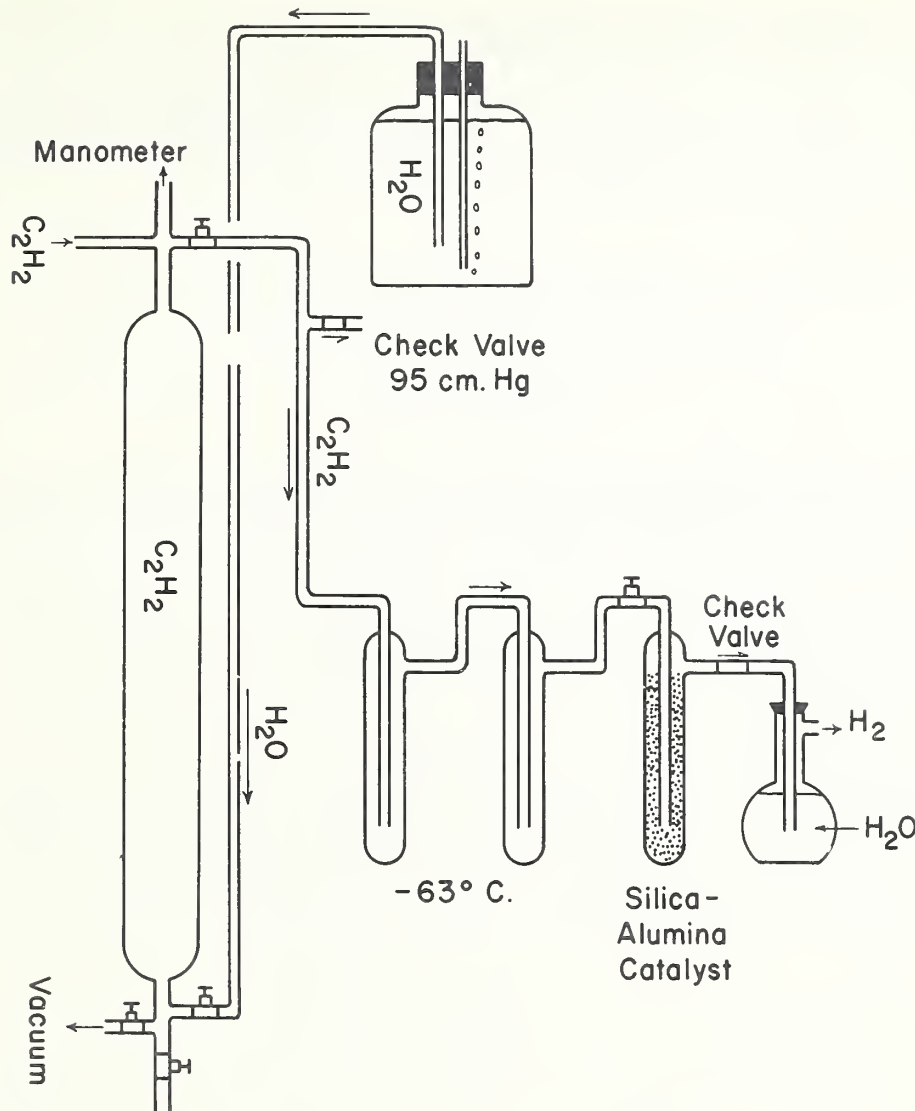
Figure 6.--Apparatus for conversion of acetylene to benzene.

## Extraction of Benzene from the Reacted Silica-Alumina Catalyst

Benzene is removed from the reacted silica-alumina catalyst by heating and evacuating the column. The column is placed in a tube-type furnace (room temperature) and connected to a small cold trap using a Teflon quick-connector union. The extraction manifold (cold traps, connectors, and column end) is evacuated and purged with dry helium. A Dewar flask containing liquid nitrogen is placed under the $C_6H_6$ freeze-out trap and the column stopcock is opened for the $C_6H_6$ withdrawal. The temperature of the furnace is raised to approximately $100^\circ$ C. to expedite the extraction. After about 15 minutes the pumping is halted and dry He is introduced slowly to the column to a positive pressure of about 25 cm. Hg. Pumping is then continued; alternate pumping and He purging are repeated twice more during the $C_6H_6$ extraction. Usually 45 minutes are sufficient for the entire withdrawal procedure.

Benzene removed from the column is permitted to liquefy and is then transferred, inside a glove box, to a dry ampoule in an atmosphere of helium. The ampoule is flame-sealed for storage

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of the sample $C_6H_6$. Sealing is accomplished in three steps: (a) a vacuum-tight quick-connector brass cap is attached to the ampoule neck; (b) the ampoule is immersed in liquid nitrogen to solidify the $C_6H_6$; (c) a portion of the ampoule neck is sealed by carefully applying a gas-oxygen flame. This method has been found to be the most satisfactory for the storage of a sample, particularly for extensive periods of time. Loss of $C_6H_6$ and possible contamination by oxygen and water are avoided by this procedure.

# RESULTS AND DISCUSSION

## Chemical Yields

The overall yield of $C_6H_6$ by this procedure is about 50 to 60 percent. Chemical yields for the individual reactions are given in table 1. The 50-percent yield of $C_6H_6$ by this procedure immediately introduces the possibility of isotopic fractionation during the synthesis, and therefore of changes in the C-14/C-12 ratio from that of the original sample. The amount of isotopic fractionation is now being investigated by mass spectrometric measurements of the C-13/C-12 ratios of the samples (10). Because the yield of $C_6H_6$ by this procedure is relatively constant, the amount of isotopic fractionation should be essentially constant between the standard and unknown samples. The fractionation effect should, therefore, largely cancel out in the final age calculations.

The chemical synthesis of $C_6^{14}H_6$ is now employed on a routine basis at the USDA Sedimentation Laboratory. Compared to the chemical procedures required for acetylene gas counting methods, only two additional chemical steps are necessary for the production of benzene. The time required for chemical conversion of a sample to benzene depends primarily on the amount of chemical pretreatment. Wood samples can usually be converted to $C_6^{14}H_6$ in three man-days. Peat and soil samples require more time. Usually, a sample can be converted to benzene and counted in one week.

TABLE 1. --Carbon yields in the conversion of carbon dioxide to benzene

| Reaction | Yield |
|---|---|
| | Percent |
| Sample + $O_2 \longrightarrow CO_2 + H_2O$ | |
| $CO_2 + 2NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$ | |
| $(NH_4)_2CO_3 + SrCl_2 \longrightarrow SrCO_3 + 2NH_4Cl$ | 95 to 100 |
| $2SrCO_3 + 5Mg^o \longrightarrow SrC_2 + SrO + 5MgO$ | |
| $SrC_2 + H_2O \longrightarrow C_2H_2 + SrO$ | 90 |
| $3C_2H_2 \xrightarrow[\text{silica-alumina}]{B_2H_6\text{-activated}} C_6H_6$ | 60 to 65 |
| Overall yield | 50 to 60 |

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# Counting Results

Counting is performed in a Packard Liquid Scintillation Spectrometer (Model 314AS) operating at 52 percent efficiency. The National Bureau of Standards' benzoic acid-$C^{14}$ standard is used as the reference standard for the efficiency measurements. Background and efficiency measurements are made after each sample to assure the stability of the counting system.

The details of the counting method and comparative results will be presented in a later paper. However, it can be stated that the quality of the benzene synthesis procedure is well illustrated by the agreement of our analyses, for both contemporary samples and "check" samples, with other $C^{14}$ dating laboratories. The unknown "check" samples were analyzed and supplied to us by laboratories employing different chemical and counting procedures, i.e., $CO_2$ or $C_2H_2$ gas proportional counters.

Absolute specific activity values for contemporary $C^{14}$ samples are presented in table 2. The values listed are in agreement with values reported by other laboratories (19, 35) for 19th century wood (reference year--1950 A.D.) and for the National Bureau of Standards' contemporary oxalic acid-$C^{14}$ standard.

TABLE 2. --Absolute specific activity of contemporary carbon-14

[Values based on $C^{14}$ half-life of 5,570 years, using 1950 A.D. as reference year]

| Sample description | Age | Specific activity [1] | Standard deviation [1] |
|---|---|---|---|
| | Years | d/m/g | d/m/g |
| Oak from Texas | [2] 1850-1854 | 12.8 | 0.2 |
| Oak from Missouri | [2] 1890-1900 | 12.9 | .2 |
| Oxalic acid, NBS contemporary $C^{14}$ standard | | 13.5 | .2 |

[1] Disintegrations per minute per gram.
[2] From tree rings.


# HANDLING DIBORANE

The hazards (toxicity, fire, and explosion) of handling $B_2H_6$ are well appreciated by the researchers in radiocarbon dating. Noakes, Isbell, and Hood (30) used commercial-cylinder $B_2H_6$ to activate the silica-alumina. The authors are aware of only one commercial source of $B_2H_6$, namely Callery Chemical Co., Callery, Pa. The cylinder $B_2H_6$ must be stored at a low temperature, preferably $-20^{\circ}$ C. or lower, to prevent its breakdown to hydrogen and higher-molecular-weight boron hydrides. The cylinders are usually stored in freezers ($-40^{\circ}$ C.) or at the temperature of dry ice ($-78^{\circ}$ C.). A special manifold or transfer system is required for releasing the $B_2H_6$ to the silica-alumina.

Carbon-14 laboratories not having access to commercial $B_2H_6$, or those laboratories not desiring to purchase this $B_2H_6$ and thus provide adequate storage and handling equipment, may find the present procedure for $B_2H_6$ generation useful in their laboratories. The generating and activating equipment, including columns for containing the silica-alumina, can be fabricated using conventional laboratory glass blowing facilities. The method described herein has been used, without accident, for activating more than 100 columns.

A concise report, including references, on the chemical and physical properties of diborane is available from the Callery Chemical Co. (1). A separate bulletin on suggested procedures for handling diborane is also available (2). The reader is urged to study these reports thoroughly before undertaking the production of diborane.

# SUMMARY

Benzene, an ideal solvent for scintillation counting, has been synthesized from original-sample carbon. The method of benzene synthesis described herein is routinely used in the radio-carbon dating program at the USDA Sedimentation Laboratory.

Benzene of scintillation purity is synthesized from samples of geomorphologic interest by the following reactions:

1. Combustion of the sample to evolve $CO_2$.

2. Absorption of the evolved $CO_2$ in $NH_4OH$.

3. Precipitation of $SrCO_3$ by the addition of $SrCl_2$ to the $(NH_4)_2CO_3$ solution.

4. Reduction of the $SrCO_3$ to $SrC_2$ by Mg metal.

5. Production of $C_2H_2$ by hydrolysis of $SrC_2$.

6. Production of $B_2H_6$, and subsequent activation of the silica-alumina, by the reaction of $NaBH_4$ and $BF_3(C_2H_5)_2O$ in an inert atmosphere.

7. Conversion of $C_2H_2$ to $C_6H_6$ by the catalytic process employing $B_2H_6$-activated silica-alumina.

The detailed procedure and apparatus described herein for the laboratory production of $B_2H_6$ can be readily adopted by laboratories not having access to commercial $B_2H_6$, or not having the interest and facilities for storing and handling large quantities of commercial-cylinder $B_2H_6$.

Benzene is produced in an overall yield of 50 to 60 percent. All of the carbon contained in the $C_6H_6$ molecule is obtained from the original-carbon sample. The large amount of sample carbon per small unit volume (or mass) of solvent provides an ideal solution for liquid scintillation counting.

# ACKNOWLEDGMENTS

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